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CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.—No. 2.

# *THE ELECTRICAL CONDUCTIVITY OF VERY DILUTE HYDROCHLORIC AND NITRIC ACID SOLUTIONS.*

BY H. M. GOODWIN AND R. HASKELL.

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CONTENTS.



## I. Purpose of the Investigation.

It is well known that there is great difficulty in obtaining an exact value for the equivalent conductivity of completely dissociated acids, owing to the large effect of the impurities of the water on the conductivity of even strong acids in very dilute solutions. These give rise to a maximum value of the conductivity at a dilution of from 500 to 2000 liters, and to a marked decrease in its value at greater dilutions. Yet a knowledge of the theoretical limiting value is of great importance, since upon it is based the assumed value of the equivalent conductivity of the hydrogen ion and the calculated degrees of dissociation of acids in general.

Kohlrausch† in 1898 derived values for the conductivity of strong acids at extreme dilution by adding to the observed value at 0.001 normal a quantity equal to the product of the observed increase between 0.001 and 0.00001 normal in the case of neutral salts by the ratio of the

* The following investigation has been made possible through financial aid extended by the Trustees of the Wm. E. Hale Research Fund.

† Wied. Ann., **66**, 794 (1898).

increase between 0.1 and 0.001 normal in the case of the acids to the corresponding increase in the case of neutral salts, the conductivity of the water having been first subtracted in all cases. By subtracting from these values the conductivity of the negative ions, which had been derived from the conductivity and transference values of neutral diionic salts, he arrived at the value 318 for the equivalent conductivity of the hydrogen ion at 18° C. — a value, however, which he regards only as a rough estimate. Three years later * he deduced also the temperature change of this conductivity, expressing it by the equation:

$$\Lambda_t = 318\,[1 + 0.0154\,(t - 18) - 0.000033\,(t - 18)^2].$$

Quite recently Noyes and Sammet † have deduced the equivalent conductivity of the hydrogen ion by an independent method; namely, by combination of the transference number of moderately dilute hydrochloric acid with the equivalent conductivity of the chlorine ion derived from transference determinations and conductivity measurements of potassium chloride. The value thus obtained is 330 at 18° or 3.8 per cent greater than that of Kohlrausch. The authors consider that this divergence cannot be due to experimental errors, but that it must arise either from an error in the extrapolated values of the conductivity of acids at extreme dilution, or from some real defect in the theoretical considerations from which the identity of the results of the two methods is predicted.

As it seemed possible to eliminate to a great extent the effect of the impurities in the water by appropriate measurements of the conductivity of dilute acids and a treatment of the data by certain methods to be described below, we undertook an investigation in this direction, both with nitric and with hydrochloric acid, and desire now to present the results which have been obtained. It may be stated in advance that these results are in substantial agreement with the extrapolated value of Kohlrausch.

## II. Preparation of the Solutions.

In the preparation of the solutions, water was used which had a specific conductance of $0.8 - 1.5 \times 10^{-6}$ reciprocal ohms and which had been purified by redistillation of ordinary distilled water to which alkaline permanganate was added, the first and last portions of the distillate

* Sitzungsberichte der Preuss. Akad. d. Wissenschaften, 1901, 1026.

† Journ. Amer. Chem. Soc., **24**, 965 (1902); **25**, 165 (1903). Zeitschr. phys. Chem., **43**, 49 (1903).

being rejected. The acid solutions were made by adding to definite portions of this water weighed portions of a standard acid of strength about 0.01-normal. The standard hydrochloric acid solution was obtained by absorbing in water hydrogen chloride gas made from twice-precipitated sodium chloride and pure sulphuric acid. Its strength was determined gravimetrically by precipitating with silver nitrate and weighing the silver chloride in Gooch crucibles. The several determinations made showed an average deviation from the mean value of less than 0.05 per cent. A standard nitric acid solution approximately 0.01 normal was made by diluting chemically pure acid through which air had been drawn to remove any lower oxides of nitrogen dissolved in it. This was standardized against barium hydroxide solution, whose strength had been determined by two independent methods. Five 0.01 normal solutions of potassium chloride were used to obtain the cell-constant; these were made from a sample of the salt which had been twice precipitated with pure hydrochloric acid and then crystallized from water, dried, and ignited to incipient fusion. A 0.01 normal sodium chloride solution made from salt prepared in the same way was used as a check.

In all cases, for the sake of greater convenience and accuracy, the content of the solution was determined by weighing, and not by volume measurement; but the values thus obtained of the number of milli-equivalents of solute in 1000 grams of water were invariably (both in the calculation of the cell-constant and of the specific and equivalent conductivity of the acid solutions) considered to be numerically identical with the concentration in milli-equivalents per liter of solution. That no appreciable error (not even one as great as 0.05 per cent) is introduced by this assumption will be readily seen, since none of the solutions were stronger than 0.01 normal.

## III. The Conductivity Apparatus and Method of Measurement.

The conductance of the solutions was measured by the Wheatstone slide-wire bridge arrangement in the form recommended by Kohlrausch, using an alternating current produced by an induction coil and a telephone as an indicator of zero potential. The bridge consisted of a marble drum on which was wound five meters of manganine wire. Five or six settings were made for each solution, so as to eliminate as far as possible any personal error in determining the exact point corresponding to the minimum sound in the telephone. The average deviation of the

separate values from the mean was less than 0.1 per cent except in the case of the extreme dilutions, where it amounted in a few cases to 0.3 per cent. The probable error of the mean was always less than 0.1 per cent except in the case of water. Both the slide-wire and the rheostat used were carefully calibrated, and the corrections were found in no case to exceed 0.1 per cent. The resistance vessel for holding the solution whose conductance was to be measured was a platinum cylinder 15 cm. high and 5 cm. in diameter. Into this was inserted, so as to rest on the bottom of the cylinder, an inverted glass bell 4.4 cm. in diameter attached to a glass tube sealed near the bottom, as shown in Figure 1.

FIGURE 1.

Into the bell an unplatinized but mechanically roughened platinum disk was sealed by means of a stiff platinum wire. The electrode was not platinized, so as to reduce as far as possible absorption effects. It had an area of 15 sq. cm., and the distance between its lower surface and the bottom of the platinum cylinder was 1.9 cm. There was enough space along the side of this disk to allow the liquid to pass, and near the top of the bell a large hole was blown so that raising and lowering the glass plunger gave an efficient means of stirring. It was proved that the "cell constant" of the apparatus varied less than 0.05 per cent with different settings of the plunger in the vessel. The use of a platinum vessel made it possible to collect the water at a little below the boiling temperature as it came off fresh from the still, whereby better water could be obtained, as there was less chance for the absorption of carbon dioxide. The plunger passed through a vulcanite cap which fitted the top of the cylinder, and thus kept the solution from much contact with the air. The cylinder was immersed almost to the top in a thermostat kept always within 0.02° of 18°. The temperature was measured by a thermometer that had been standarized and corrected to the scale of an air thermometer. The room was also kept nearly at the same temperature to prevent condensation at the top of the cell. Contacts were made by mercury.

The solutions were made by adding successively a number of portions of standard acid (approximately 0.01 normal) from a weighed Beckman pipette to a weighed quantity (about 180 grams) of water in the vessel. The weight of the added portion could easily be determined to less

than 0.5 milligram, or 0.05 per cent in the case of the smallest portion. In this way a series of solutions, usually varying in concentration from about 0.0001 normal up to 0.001 or 0.002 normal, were prepared, and their conductance measured.

Several experiments were made to determine whether the conductivity of dilute acid solutions changed with time upon standing in the covered conductivity vessel in the thermostat. The change upon standing over night amounted to only 0.1 per cent of the conductivity of a 0.0002 normal solution.

In order to confirm the accuracy of the method, similar series of measurements were made with potassium chloride solutions at the same dilutions as in the case of the acids. The results, which are communicated in the Section V, agree within 0.1 per cent with those obtained by Kohlrausch and Maltby, in their very accurate determinations published in 1900.*

## IV. Methods of Correcting for Impurities in Water at Great Dilution.

We have employed two methods for eliminating the influence of the impurities in the water on the conductivity of the acid solutions. Both of these involve the principle that *the total effect of the acid and of the impurities in the water on the conductivity of each other is already produced when a relatively small quantity of acid has been added to the water, after which further additions of acid remain unaffected by the impurities.*

In the first method of computation this principle is applied in a direct manner by simply subtracting the conductivity of a very dilute acid solution from that of a more concentrated one, and regarding the ratio of this difference to the difference in the respective concentrations as the equivalent conductivity of the acid at the higher concentration; that is, if $\kappa_1$ and $\kappa_2$ are the conductivities at the concentrations $C_1$ and $C_2$ respectively, $C_1$ being a very small concentration, it is assumed that $\frac{\kappa_2 - \kappa_1}{C_2 - C_1} = \Lambda_{C_2}$, the equivalent conductivity at the concentration $C_2$.†

* Wissensch. Abhandlungen d. phys.-technischen Reichsanstalt, **3**, 157–227 (1900). Zeitschr. phys. Chem., **36**, 750 (1901).

† In the calculation of $\Lambda_{C_2}$ it is necessary to apply a slight correction to the observed conductance ($\kappa_1'$), since when the second portion of acid is added the

Thus, the underlying idea is the preparation, by the addition of a little acid, of a sample of solvent the impurities in which shall have no appreciable influence on the conductivity of subsequently added portions of acid. Theoretically, it seems highly probable that this must be practicable; for any basic constituents of the water like ammonium or other alkaline hydroxides or carbonates would be completely neutralized, and any weakly acid constituent like carbonic acid which Kohlrausch * has shown to be undoubtedly the chief source of impurity, would have its dissociation reduced nearly to zero, as soon as the concentration of the strong acid added reached a value as great as, or a few times greater than, the concentration of the impurity. It is true that even though the impurities may have been thus rendered harmless, the increase in conductivity produced by the added portion of acid will not be strictly identical with the conductivity which it would have if it were added to pure water; for the acid originally present will be somewhat reduced in dissociation, and will itself reduce the dissociation of the added acid: but this effect is known to be very small at high dilutions, and the last-mentioned part of it is eliminated by regarding the calculated equivalent conductivity as corresponding to the final concentration rather than to the difference in concentration.†

In regard to the choice of the initial concentration, it may be pointed out that this must be taken so large that the maximum effect of the impurities in the water and of the acid on the conductivity of each other shall be attained, and that this condition is shown to be fulfilled when the equivalent conductivities calculated from two successive values of the initial concentration are in substantial agreement. The fact that

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volume of the solution is somewhat increased, whereby the observed conductance and concentration would be decreased in the same proportion. Thus if $m_w$, $m_1$ and $m_2$ are the weights of water, of the first portion of added acid of a concentration $C_0$, and of the second portion respectively, then, placing volumes proportional to weights, which at the dilutions in question produces no error, we have:

$$\kappa_1 = \kappa'_1 \frac{m_w + m_1}{m_w + m_1 + m_2}. \quad \text{Also} \quad C_2 - C_1 = \frac{C_0 m_2}{m_w + m_1 + m_2}.$$

* Wissensch. Abhandlungen d. phys.-tech. Reichsanstalt, 3, 193 (1900).

† For example, it is readily calculated from Kohlrausch's mean values (Wied. Ann., 66, 794, 1898) of the change of the conductivity at 18° of the ions of neutral salts with the dilution that the mean error in their equivalent conductivity would be 0.42 per cent at 0.0002 normal and 0.25 per cent at 0.0005 normal if computed by the method here described, taking 0.0001 as the initial concentration. In the case of the strong acids, whose conductivity changes much less rapidly with dilution, the error from this source would be about one-half as great.

such an agreement is actually found to exist even with relatively small values of the initial concentration is evidence of the correctness of the principle on which the computation is based.

The second method of computation is based on the assumption that the true values of the equivalent conductivity increase regularly to a maximum at the highest dilution, and that the decrease in the observed values from the maximum obtained at a moderate dilution is due to a *constant* error in the specific conductance arising from the effect of the impurities in the water. Therefore it is justifiable to add to the observed values of the specific conductance such a quantity as will cause

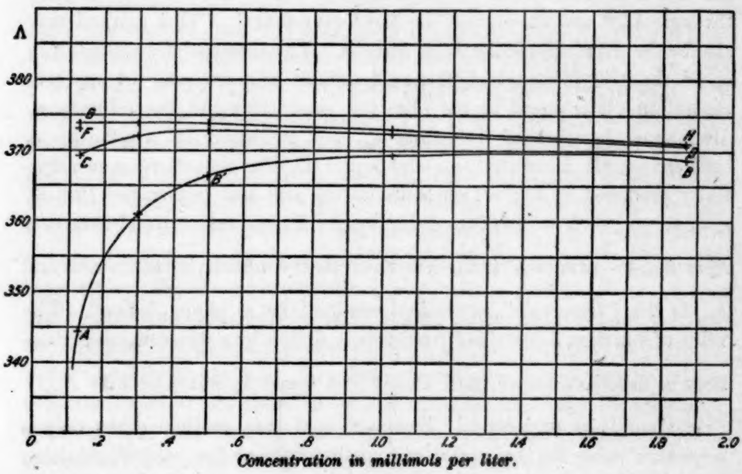


FIGURE 2.

the maximum in the so-corrected equivalent conductivity values to occur at the lowest concentration at which the error just referred to has attained its constant value. The method of procedure is best illustrated by a reference to the accompanying diagram (Figure 2). In this the curve AB represents the "observed" values of the equivalent conductivity Λ, of the acid computed from the results of an actual series of experiments (first series, in nitric acid, page 410) by subtracting from the observed specific conductivity of the solution $\kappa_s$ the observed conductivity of the water $\kappa_w$, and dividing the difference by the concentration $c$; that is, $\Lambda_{Obs} = (\kappa_s - \kappa_w) / c$. Now the error in the value Λ at A must be at least as great as the ordinate AC, $C$ being equal to the

maximum ordinate of AB. If we therefore increase its value by this amount and increase the observed value of A of every other point as B′ by this amount multiplied by the inverse ratio of the concentrations corresponding to B′ and A respectively, a new series of values corresponding to the curve CD is obtained. The value $C$ is still seen to be in error by an amount as great as CF (F being equal again to the maximum ordinate of the new curve CD); the other values on this curve are in error by an amount less in proportion to the greater concentration to which they correspond: we therefore increase all the values in the same way as before, producing a third curve, and this process is repeated till the maximum point on the resulting curve lies on the ordinate through ACF and the curve has the form of GH. This method may also be described algebraically as follows. The true specific conductivity $\kappa_c$, of the acid (that which it would exhibit in pure water at any concentration $c$), is equal to the observed conductivity of the solution $\kappa_s$, diminished by that of the water $\kappa_w$, and increased by a quantity $\delta$, constant at all concentrations and equal to the reduction in conductivity produced by mutual influence of the acid and impurities; that is, $\kappa_c = \kappa_s - \kappa_w + \delta$, or expressed in terms of equivalent conductivities, $\Lambda_c = \Lambda_{obs} + \frac{\delta}{c}$ where $\Lambda_c$ is the true equivalent conductivity of the acid and $\Lambda_{obs}$ is the "observed" equivalent conductivity as above defined. The value of $\delta$ is then determined from this equation by a series of approximations as described above until finally $\frac{\delta}{c} = 0$ and $\Lambda_c$ coincides with $\Lambda_{obs}$.

It should be understood, however, that this method gives only a minimum value for the equivalent conductivity at the highest dilution, for it is only in case the Mass-Action Law equation holds that the conductivity curve approaches asymptotically to a maximum with increasing dilution. If the empirical formula of Kohlrausch $\Lambda_0 - \Lambda_c = KC$ is applicable, the upward slope of the curve must continually increase with decreasing concentration. In fact, Kohlrausch found that the behavior of neutral salts at very low concentrations (0.001 — 0.0001 normal) was intermediate between that required by these two formulae. The values extrapolated with the help of the cube-root formula will therefore give in all probability a maximum limit for the conductivity at the greatest dilution, and the true value will lie between it and that derived by the method just described.

In applying these methods to our results, from 0.06 to 0.1 milli-equivalents per liter was taken as the standard initial concentration,

although some measurements and computations have also been made at greater dilutions. The reasons for this selection are: first, that the resistance measurements, owing to a sharper minimum, are considerably more accurate (the average deviation of the separate readings from the mean being less than 0.1 per cent) than in the more dilute solution; and secondly, that the computed equivalent conductivities differ when the initial concentration chosen is varied from less than 0.03 to 0.06 millinormal, but that they no longer do so to an important extent when it is varied from 0.05 to 0.01 millinormal, showing that in the 0.03 millinormal solution the maximum influence of the water has not yet been produced.

It will be seen from the data given in the next section that the water used in different series of experiments had a conductivity varying from 0.8 to $1.6 \times 10^{-6}$, and consequently, the observed equivalent conductivity at the higher dilutions also exhibit considerable variations. In fact, the latter exist even where different samples of water with the same conductivity were used, showing that the character of the impurities varies and exerts a specific influence. Nevertheless, the corrected values of the equivalent conductivity are substantially identical — a fact which furnishes strong evidence of the correctness of the principle underlying the computations.

The above methods only serve to extend the series of reliable values of the equivalent conductivity of acids from about 0.002 normal down to 0.0002 or 0.0001 normal. To what extent the values at the latter concentration differ from those at infinite dilution can only be estimated. Probably the best basis for this estimate is the assumption of Kohlrausch which is most briefly expressed by the relation:

$$\frac{(\Lambda_{\infty} - \Lambda_{4000}) \text{ for acids}}{(\Lambda_{4000} - \Lambda_{100}) \text{ for acids}} = \frac{(\Lambda_{\infty} - \Lambda_{4000}) \text{ for salts}}{(\Lambda_{4000} - \Lambda_{100}) \text{ for salts}} = \frac{0.9}{3.0}\,*$$

This method of extrapolation has been applied to our results. Since according to our measurements with hydrochloric acid described in Sections V. and VI. $\Lambda_{4000} - \Lambda_{100} = 377.6 - 369.3 = 8.3$, the so-determined value of $(\Lambda_{\infty} - \Lambda_{4000})$ for acids is only 2.5 units (or 0.7 per cent).

## V. The Conductivity Data.

The experimental data and the values calculated therefrom will now be presented.

The temperature was in all cases 18.00° ± 0.02°. The standard

* Kohlrausch, Wied. Ann., **66**, 794 (1898).

solution of hydrochloric acid used in all the experiments was 0.009074* normal; that of nitric acid was 0.010145 † normal. The cell constant or capacity of the resistance vessel (that is, the ratio of the specific conductance of any solution to its actual conductance as measured in the vessel) was 0.11659.‡

The following tables contain the results of the separate series of experiments. As headings are given, the weight in grams ($m_w$) of water taken, its actual conductance ($L_w$) multiplied by $10^6$ when measured in the vessel, and its specific conductance ($\kappa_w$) multiplied by $10^6$. The first column gives the number of the portions of standard acid or potassium chloride solution which were added; the second gives the total weight of the added portions; the third, the concentration ($c$) of the resulting solution in milliequivalents per liter (see Section II); the fourth, the conductance in reciprocal ohms measured in the resistance vessel and multiplied by $10^6$; the fifth, the equivalent conductivity of the acid calculated by subtracting from the specific conductance of the solution ($\kappa_s$) that of the water and dividing the difference by the concentration i. e. $(\kappa_s - \kappa_w)/c$. In the sixth and seventh columns are given the corrected values of the equivalent conductivity computed by the first method described in Section IV, taking for the initial concentration that corresponding to the first and second added portions, respectively. In the eighth column are given the corrected values of the equivalent conductivity calculated by the second method described in Section IV. (In the case of the potassium chloride series these are replaced by the equivalent conductivities obtained by Kohlrausch and Maltby.)

* This result was based upon four determinations, of which the data were as follows:

| | | | | |
|---|---|---|---|---|
| Grams HCl solution taken | 346.27 | 328.60 | 347.70 | 356.38 |
| Grams AgCl obtained | 0.4506 | 0.4277 | 0.4521 | 0.4623 |
| Equivalents per 1000 grams sol. | 0.009076 | 0.009078 | 0.009068 | 0.009047 |

The last on account of its great deviation was omitted in taking the mean.

† This solution was obtained by dilution (by weight), of a 0.05 normal solution which has been standardized against a 0.1 normal solution of recrystallized barium hydroxide, the titration values showing an average deviation of 0.03 per cent from their mean. The barium hydroxide was standardized by neutralizing it with nitric acid, evaporating, drying at 170°, and weighing as $Ba(NO_3)_2$, and also precipitating it with sulphuric acid, filtering out, igniting, and weighing the $BaSO_4$. The average deviation from the mean of the four determinations by those two methods was 0.05 per cent.

‡ This was the mean derived from measurements with five distinct 0.01 normal potassium chloride solutions containing 0.7455 grams KCl weighed in air, in 1000 grams water: the average deviation of the five values from the mean was 0.03 per cent.

### Hydrochloric Acid.

$m_w = 163.73$; $10^6\, L_w = 11.13$; $10^6\, \kappa_w = 1.30$.

| Portion No. | Total Weight of Added Portions. | Concentration in Milliequivalents per Liter. | Observed Conductance × $10^6$. | Equivalent Conductivity. | | | |
|---|---|---|---|---|---|---|---|
| | | | | Water Subtracted. | By First Method. I. | By First Method. II. | By Second Method. |
| 1 | 0.2248 | 0.0125 | 34.82 | 221.8 | . . . | . . . | 420.6 |
| 2 | 2.0305 | 0.1114 | 349.34 | 354.6 | 371.3 | . . . | 376.9 |
| 3 | 5.0528 | 0.2717 | 868.42 | 367.9 | 374.8 | 376.8 | 376.9 |
| 4 | 8.2065 | 0.4341 | 1390.9 | 371.3 | 375.7 | 377.8 | 376.9 |
| 5 | 12.9987 | 0.6689 | 2144.8 | 372.6 | 375.4 | 376.1 | 376.2 |
| 6 | 19.190 | 0.9574 | 3061.0 | 371.4 | 375.4 | 375.7 | 374.0 |
| $m_w = 170.96$; $10^6\, L_w = 11.95$; $10^6\, \kappa_w = 1.37$. | | | | | | | |
| 1 | 1.3360 | 0.07036 | 221.3 | 346.8 | . . . | . . . | 379.6 |
| 2 | 5.4563 | 0.2806 | 904.3 | 370.6 | 378.5 | . . . | 376.4 |
| 3 | 9.6226 | 0.4835 | 1557.9 | 372.7 | 377.0 | . . . | 376.3 |
| 4 | 12.032 | 0.5966 | 1923.8 | 373.6 | 377.0 | . . . | 376.4 |
| 5 | 17.928 | 0.8612 | 2775.5 | 374.1 | 376.4 | . . . | 375.9 |
| 6 | 37.166 | 1.6204 | 5214.8 | 374.3 | 375.4 | . . . | 375.3 |
| $m_w = 193.83$; $10^6\, L_w = 9.41$; $10^6\, \kappa_w = 1.10$. | | | | | | | |
| 1 | 0.5642 | 0.02634 | 76.56 | 297.1 | . . . | . . . | 382.8 |
| 2 | 1.2787 | 0.05947 | 183.82 | 341.8 | 377.2 | . . . | 379.5 |
| 3 | 2.4332 | 0.1125 | 354.3 | 357.4 | 375.6 | 374.4 | 377.5 |
| 4 | 5.0564 | 0.2307 | 737.5 | 367.9 | 376.8 | 376.8 | 377.6 |
| 5 | 7.3884 | 0.3311 | 1062.2 | 370.7 | 377.0 | 376.9 | 377.3 |
| 6 | 11.162 | 0.4942 | 1588.8 | 372.6 | 376.7 | 376.7 | 377.0 |
| 7 | 15.184 | 0.6593 | 2119.6 | 373.1 | 376.1 | 376.2 | 376.3 |
| 8 | 35.180 | 1.3942 | 4489.5 | 374.6 | 376.0 | 375.9 | 376.2 |
| $m_w = 184.65$; $10^6\, L_w = 7.44$; $10^6\, \kappa_w = 0.868$. | | | | | | | |
| 1 | 2.0218 | 0.09828 | 313.9 | 363.5 | . . . | . . . | 378.7 |
| 2 | 3.8508 | 0.1854 | 597.8 | 371.3 | 379.8 | . . . | 379.4 |
| 3 | 5.7913 | 0.2760 | 889.8 | 372.8 | 377.7 | 375.7 | 378.1 |
| 4 | 8.1604 | 0.3841 | 1238.7 | 373.7 | 377.1 | 376.0 | 377.5 |
| 5 | 11.665 | 0.5392 | 1741.3 | 374.9 | 377.3 | 376.8 | 377.6 |
| 6 | 18.686 | 0.8319 | 2678.1 | 374.3 | 375.6 | 375.1 | 376.1 |
| $m_w = 184.65$; $10^6\, L_w = 7.29$; $10^6\, \kappa_w = 0.854$. | | | | | | | |
| 1 | 0.9254 | 0.04526 | 141.28 | 345.1 | . . . | . . . | 371.6 |
| 2 | 2.5137 | 0.1219 | 392.35 | 368.3 | 381.9 | . . . | 378.3 |
| 3 | 5.4093 | 0.2583 | 835.20 | 373.7 | 379.8 | 378.4 | 378.4 |
| 4 | 7.8974 | 0.3722 | 1201.8 | 374.2 | 378.1 | 376.9 | 377.4 |
| 5 | 11.571 | 0.5351 | 1728.0 | 374.9 | 377.5 | 376.8 | 377.2 |
| 6 | 15.715 | 0.7117 | 2298.5 | 375.3 | 377.2 | 376.7 | 376.9 |
| 7 | 19.915 | 0.8834 | 2848.5 | 374.9 | 376.5 | 375.9 | 376.2 |
| 8 | 40.055 | 1.6176 | 5208.0 | 374.8 | 375.6 | 375.4 | 375.5 |

## Nitric Acid.

$m_w = 181.38$; $10^6\ L_w = 13.35$; $10^6\ \kappa_w = 1.59$.

| Portion No. | Total Weight of Added Portions. | Concentration in Milliequivalents per Liter. | Observed Conductance $\times 10^6$. | Equivalent Conductivity. Water Subtracted. | By First Method. I. | By First Method. II. | By Second Method. |
|---|---|---|---|---|---|---|---|
| 1 | 0.8480 | 0.0472 | 132.1 | 293.0 | . . . | . . . | 374.6 |
| 2 | 2.3534 | 0.1299 | 397.0 | 344.1 | 373.1 | . . . | 373.9 |
| 3 | 5.4994 | 0.2985 | 937.7 | 360.9 | 373.4 | 373.6 | 373.9 |
| 4 | 9.3059 | 0.4951 | 1568.1 | 366.1 | 373.5 | 373.6 | 373.8 |
| 5 | 20.477 | 1.0291 | 3273.2 | 369.3 | 372.6 | 372.6 | 373.0 |
| 6 | 40.940 | 1.8679 | 5922.0 | 368.8 | 371.4 | 371.3 | 370.8 |
| $m_w = 175.49$; $10^6\ L_w = 13.05$; $10^6\ \kappa_w = 1.52$. | | | | | | | |
| 1 | 1.0421 | 0.0599 | 183.7 | 332.0 | . . . | . . . | 374.4 |
| 2 | 3.2765 | 0.1860 | 588.9 | 361.0 | 374.7 | . . . | 374.7 |
| 3 | 6.5193 | 0.3634 | 1159.7 | 367.9 | 374.7 | 374.8 | 374.7 |
| 4 | 9.0405 | 0.4972 | 1586.0 | 368.8 | 373.8 | 373.5 | 373.9 |
| 5 | 14.931 | 0.7955 | 2538.4 | 370.1 | 373.0 | 372.7 | 373.2 |
| 6 | 20.373 | 1.0553 | 3368.2 | 370.6 | 372.8 | 372.6 | 373.0 |
| $m_w = 169.23$; $10^6\ L_w = 12.03$; $10^6\ \kappa_w = 1.40$. | | | | | | | |
| 1 | 1.8262 | 0.1083 | 337.8 | 350.6 | . . . | . . . | 375.2 |
| 2 | 4.1137 | 0.2465 | 782.5 | 364.4 | 375.1 | . . . | 375.2 |
| 3 | 7.0453 | 0.4110 | 1306.2 | 367.9 | 373.9 | . . . | 374.4 |
| 4 | 12.1903 | 0.6868 | 2190.6 | 369.8 | 373.2 | . . . | 373.7 |
| 5 | 19.894 | 1.0720 | 3421.2 | 370.8 | 372.9 | . . . | 373.4 |
| 6 | 40.299 | 1.9550 | 6229.7 | 370.2 | 371.8 | . . . | 371.6 |
| $m_w = 183.75$; $10^6\ L_w = 12.64$; $10^6\ \kappa_w = 1.48$. | | | | | | | |
| 1 | 1.6063 | 0.0879 | 277.1 | 350.7 | . . . | . . . | 372.1 |
| 2 | 3.7972 | 0.2054 | 656.0 | 365.2 | 373.9 | . . . | 374.1 |
| 3 | 5.8714 | 0.3141 | 1005.6 | 369.5 | 375.3 | 374.8 | 374.2 |
| 4 | 8.8942 | 0.4684 | 1500.0 | 370.2 | 374.6 | 374.1 | 374.1 |
| 5 | 14.166 | 0.7261 | 2325.0 | 369.6 | 373.9 | 373.6 | 372.2 |
| 6 | 20.282 | 1.0085 | 3224.0 | 371.2 | 373.1 | 372.8 | 372.8 |
| 7 | 40.360 | 1.8270 | 5827.7 | 371.0 | 371.9 | 371.5 | 372.0 |

## Potassium Chloride.

$m_w = 185.22$; $10^6\ L_w = 0.862$; $10^6\ \kappa_w = 1.006$.

Conc. Stand. Solution = 0.009990.

| | | | | | | | (Kohlrausch and Maltby.) |
|---|---|---|---|---|---|---|---|
| 1 | 1.2147 | 0.0651 | 80.66 | 129.02 | . . . | . . . | 129.16 |
| 2 | 3.5447 | 0.1876 | 215.62 | 128.64 | 128.52 | . . . | 128.81 |
| 3 | 9.9054 | 0.5072 | 565.55 | 128.06 | 127.99 | . . . | 128.10 |
| 4 | 20.108 | 0.9784 | 1078.2 | 127.45 | 127.46 | . . . | 127.39 |

In connection with the above data, attention is called to the close agreement in the case of potassium chloride between our values of the equivalent conductivity, given in column five marked "water subtracted," with those of Kohlrausch and Maltby; also to the fact that the application of the first correction method to this neutral salt causes a change of less than 0.1 per cent in the values of the equivalent conductivity. It will be seen, on the other hand, that, in the case of the acids, both methods of computation raise the equivalent conductivity on an average by about 2 per cent in 0.25 millinormal, and by about 0.5 per cent in millinormal solution. Although the values in column five vary quite widely in the different series owing to differences in the quality of the water used, yet when corrected by Method I they are in substantial agreement in all cases where the concentration corresponding to the first added portion exceeds 0.05 millinormal. The agreement between the results obtained by the two methods is considered on page 413.

The mean of the "water-subtracted" values at the concentration millinormal (374.0 for hydrochloric acid and 371.4 for nitric acid) are nearly one per cent lower than the corresponding values earlier obtained by Kohlrausch* (377 and 375 respectively). This fact led us to make a new series of measurements on the conductivity of hydrochloric acid at higher concentrations. These were made at 18° in a U-shaped apparatus with a new sample of acid prepared and standardized as before.† The dilutions of the stock solution (0.13747 normal) were made by weight and reduced to volume-concentrations at 18°, by means of the specific gravities of water and of the stock solution. On account of the wide range of concentrations measured it was found necessary to use two resistance vessels. The cell constants or capacities of these, determined by five 0.01 normal potassium chloride solutions, were 2.5417 and 8.5370. The average deviation of the separate values from the mean was less than 0.03 per cent in each case.

The results are contained in the following table. Values corresponding to the round concentrations are summarized in Section VII (page 415).

The values are seen to be only slightly (0.1–0.4 per cent) lower than

* Kohlrausch and Holborn, Leitvermogen der Electrolyte, p. 160.

† The analytical data were as follows:

| | | | |
|---|---|---|---|
| Grams HCl solution taken . . . | 112.34 | 106.58 | 91.31 |
| Grams AgCl obtained . . . . . | 2.2121 | 2.0988 | 1.7994 |
| Equivalents per 1000 grams sol. . | 0.13734 | 0.13734 | 0.13744 |

Hydrochloric Acid.

$10^6 L_w = 0.34$. $10^6 \kappa_w = 0.85$. Cell constant = 2.542.

| Concentration in Equivalents per Liter. | Actual Conductance $\times 10^6$. | Equivalent Conductivity.* | Equivalent Conductivity (interpolated from Kohlrausch). |
|---|---|---|---|
| 0.001917 | 270.12 | 375.0 | 376+ |
| 0.001937 | 285.87 | 375.1 | 376+ |
| 0.004744 | 697.25 | 373.1 | 373+ |
| 0.005525 | 809.79 | 372.5 | 372+ |
| 0.010124 | 1470.8 | 369.2 | 370 |
| 0.01147 | 1661.8 | 368.2 | 369+ |
| 0.02714 | 3878.6 | 363.4 | 365 - |
| 0.03137 | 4468.9 | 362.1 | 364– |
| $10^6 L_w = 0.10$. $10^6 \kappa_w = 0.85$. Cell constant = 8.537. | | | |
| 0.13747 | 5600.9 | 347.8 | 347+ |

those of Kohlrausch. Noyes and Sammet † found in $\frac{1}{500}$ and $\frac{1}{2000}$ normal solution values 0.5–06 per cent less than Kohlrausch's. The above values were plotted against the cube root of the concentration, and between 0.005 and 0.137 normal were found to lie upon a straight line, the greatest deviation from it being less than 0.1 per cent.

## VI. The Corrected Values of the Equivalent Conductivity.

In the following table are summarized the equivalent conductivity values of the dilute solutions computed by both methods from all the series of experiments. The values are interpolated for round concentrations intermediate between those involved in the experiments. In the case of the first method the values computed from the initial concentration corresponding to the first added portion were used, except in the cases where this was less than 0.05 millinormal.

* In these values no account is taken of the effect of the water, the correction for which is negligible, except in the first two cases in which the concentration is approximately only 0.002 normal. For this dilution the correction is +0.2 unit, making the corrected values 375.2 and 375.3 respectively. This correction is taken as one-half that computed from data on p. 409 for a 0.001 normal solution.

† Journ. Amer. Chem. Soc., **24**, 964 (1902).

### Hydrochloric Acid.

| Concentration Milliequivalents. | *First Method.* Separate Series. | | | | | Mean. | *Second Method.* Separate Series. | | | | | Mean. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.10 | . . . | . . . | . . . | . . . | . . . | . . . | 376.9 | 379.1 | 377.5 | 378.8 | 378.3 | 378.1 |
| 0.25 | 376.8 | 378.5 | 376.8 | 377.7 | 378.4 | 377.6 | 376.9 | 376.9 | 377.5 | 378.2 | 378.4 | 377.6 |
| 0.50 | 377.4 | 377.0 | 376.7 | 377.3 | 376.8 | 377.0 | 376.7 | 376.4 | 377.0 | 377.5 | 377.3 | 377.0 |
| 0.75 | 376.1 | 376.7 | 376.2 | 375.6 | 376.5 | 376.2 | 375.5 | 376.1 | 376.3 | 376.5 | 376.7 | 376.0 |
| 1.00 | 375.7 | 376.2 | 376.0 | . . . | 375.8 | 375.9 | 373.7 | 375.8 | 376.2 | 375.6 | 376.1 | 375.5 |
| 1.50 | . . . | 375.6 | 375.9 | . . . | 375.5 | 375.7 | . . . | 375.4 | 376.1 | . . . | 375.6 | 375.6 |
| **Nitric Acid.** | | | | | | | | | | | | |
| 0.10 | . . . | . . . | . . . | . . . | . . . | . . . | 374.0 | 374.6 | 375.2 | 374.1 | . . . | 374.3 |
| 0.25 | 373.6 | 374.7 | 375.1 | 374.5 | . . . | 374.5 | 373.9 | 374.7 | 375.2 | 374.1 | . . . | 374.3 |
| 0.50 | 373.6 | 373.8 | 373.7 | 374.5 | . . . | 373.9 | 373.8 | 373.9 | 374.2 | 373.8 | . . . | 373.9 |
| 0.75 | 373.1 | 373.0 | 373.1 | 373.8 | . . . | 373.3 | 373.4 | 373.3 | 373.6 | 373.4 | . . . | 373.4 |
| 1.00 | 372.6 | 372.8 | 372.9 | 373.1 | . . . | 372.9 | 373.1 | 372.9 | 373.4 | 372.8 | . . . | 373.0 |
| 2.00 | 371.1 | . . . | 371.8 | 371.7 | . . . | 371.5 | 370.4 | . . . | 371.5 | 371.9 | . . . | 371.3 |

It will be seen that the results of the two methods of calculation agree almost completely in the case of both acids. The equivalent conductivity for 0.25 millinormal hydrochloric acid is 377.6, and for nitric acid of the same strength is 374.4. The difference, 3.2, agrees well with the difference, 3.6, between the conductivities of the Cl and $NO_3$ ions as derived by Kohlrausch from measurements with neutral salts. It is also of interest to note that the conductivity value extrapolated for 0.25 millinormal hydrochloric acid from those between 0.005 and 0.137 normal under the assumption of the validity of the cube-root formula ($\Lambda_0 - \Lambda_c = K\,C^{\frac{1}{3}}$) is 381 or only about 0.9 per cent greater than our corrected value.

It remains only to apply the estimated correction of +2.5 units, dis-

cussed at the end of Section IV, in order to obtain the most probable values of the equivalent conductivity at infinite dilution. The values so obtained are 380.1 for hydrochloric acid, and 377.0 for nitric acid. The values recently derived by Kohlrausch * are 383.4 and 379.8 respectively, which differ from ours by less than 1 per cent. Unless the change with the concentration at very high dilutions follows a law radically different from that prevailing at moderate dilutions, it seems certain that these values are substantially correct. The much higher value 395.5 for hydrochloric acid derived by Noyes and Sammet from transference experiments apparently arises from some considerable error the nature of which still remains to be explained.

## VII. Summary.

In this article have been described measurements of the electrical conductivity at 18° of very dilute (0.0001 to 0.002 normal) hydrochloric and nitric acid solutions made by adding to a known weight of water successive portions of 0.01 normal acid. To eliminate the effect of the impurities of the water, two methods of computation of the equivalent conductivity have been used. In both of these, the assumption is involved that the total effect of the acid and impurities on the conductance of each other is produced when a relatively small quantity of acid has been added to the water. The experiments themselves furnish evidence of the correctness of this assumption. In the first method, the increase of the specific conductance over this initial value divided by the increase of concentration is regarded as the equivalent conductivity at the higher concentration. In the second method, such a quantity, constant at every concentration, is added to the observed values of the specific conductance as will cause the maximum in the equivalent conductivity values calculated therefrom to occur at the lowest concentration at which the total influence of the acid and impurities on each other has been produced. In spite of considerable variations in the observed conductivities due to the use of different samples of water, the corrected values of the equivalent conductivity derived from different experiments and those computed by the two methods agree well with each other. New determinations were also made at higher concentrations with hydrochloric acid. The final values of the equivalent conductivity ($\Lambda$) at various round concentrations (C) in equivalents per liter are as follows:

* Sitzungsber. d. konigl. preuss. Akad., 1901, 1031.

| Concentration in Mols. | $\Lambda_{HCl}$. | $\Lambda_{HNO_3}$. | Concentration in Mols. | $\Lambda_{HCl}$. |
|---|---|---|---|---|
| 0 | 380.1 | 377.0 | 0.005 | 372.6 |
| 0.00025 | 377.6 | 374.5 | 0.010 | 369.3 |
| 0.00050 | 377.0 | 373.9 | 0.020 | 365.5 |
| 0.00075 | 376.2 | 373.3 | 0.030 | 362.5 |
| 0.00100 | 375.9 | 372.9 | 0.05 | 358.4 |
| 0.00150 | 375.6 | | 0.100 | 351.4 |
| 0.00200 | 375.3 | | | |

The values for zero concentration or infinite dilution are extrapolated from those for 0.00025 normal under the assumption that the change between these two limits of concentration stands in the same ratio to that between 0.00025 and 0.01 normal as in the case of neutral salts; this ratio having been already derived by Kohlrausch. These values are less than one per cent lower than those of Kohlrausch and are believed to be substantially correct. That derived by Noyes and Sammet from transference experiments for hydrochloric acid (395.5), on the other hand, is, for some reason as yet unknown, four per cent higher.

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